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POLYAMIDE BLOW MOLDING METHOD

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SPECIFICATION

1. Title of the invention: Polyamide blow molding method

2. Claim

Polyamide blow molding method characterized by the fact that a modified polyamide with a molecular weight of 30,000 or more obtained by reacting a meltable polyamide that contains a terminal amino group with an N,N'-bisacyllactam is blow molded.

3. Detailed explanation of the invention

This invention pertains to a method of blow molding, particularly to a method of blow molding an appropriate specifically modified polyamide.

Normally, polyamides do not form parisons well and so cannot be blow molded. And even when specially modified polyamides are used for blow molding, the process is largely limited to small,

hollow molded articles. The quality of large molded articles produced has been unsatisfactory.

To improve the parison stability, it is necessary that the polyamide be modified to meet at least these conditions:

- 1) the polyamide should have a high viscosity; i.e., 20,000 P or higher, at temperatures near its melting point,

- 2) the temperature dependence of the polyamide melt viscosity should be as small as possible;

- 3) the melt viscosity should be high at low pressure during melt extrusion.

In addition to items 1)-3) above, for blow molding polyamide, it is preferable that:

- 4) the viscosity of the molten polyamide be very stable, and that

- 5) it not become colored when it melts.

Various methods have been proposed to impart a high viscosity to polyamides. Although highly viscous polyamides are obtained with each of them, no one of them satisfies all of the conditions 2)-5) above as required for blow molding. For example, a method in which a highly viscous polyamide is produced by melt polymerization in the presence of phosphoric acid and other polybasic acids is known (refer to the specification of U.S. Patent No. 2,557,808) but polyamides obtained with this method, even when they meet condition 1) above, have poor viscosity stability when they are melted. In addition, a method in which the polyamide is made highly viscous by a solid polymerization method has been proposed (refer to Japanese Kokoku Patent No. Sho 32[1957]-8943), but the highly viscous polyamides obtained by this method have poor viscosity stability when they

are melted, and on top of this, their melt viscosity temperature dependence is high. Furthermore, methods in which an isocyanate compound or an epoxy compound is added to the polyamide and the polyamide is made highly viscous by crosslinking have also been proposed (for example, refer to the specification of British Patent No. 1,059,930 or to Japanese Kokoku Patent No. Sho 48[1973]-7509), but the polyamides obtained tend to become colored and to gel. On top of this, as crosslinking proceeds, the temperature dependence of the melt viscosity increases.

The present inventors performed earnest research on methods by which even large polyamide molded articles could be produced by blow molding. As a result, they discovered that when specific modified polyamides are molded, satisfactory blow molded articles are obtained; thus, they perfected this invention.

In short, this invention is a polyamide blow molding method, characterized by the fact that a modified polyamide with a molecular weight of 30,000 or more which is obtained by reacting a meltable polyamide that contains a terminal amino group with a molten N,N'-bisacyllactam is blow molded.

The meltable polyamide that contains a terminal amino group which is used for this invention is a polyamide obtained by the condensation of an amino acid (or a lactam), a polyamide obtained by the condensation of a dibasic acid diamine, or even a copolymer of these. In specific terms, this includes, for example, nylon 4, nylon 6, nylon 7, nylon 9, nylon 11, nylon 12, nylon 66, nylon 69, nylon 610, nylon 612, nylon 6/66 copolymer, nylon 6/66/610 copolymer, nylon 6/6T copolymer (T represents a terephthalic acid component), nylon 6/6T/6I (I represents an

isophthalic acid component), etc. It may also be a block copolymer or a blend of two or more polyamides.

The N,N'-bisacyllactam used to modify this polyamide is a compound that can easily be synthesized by a condensation reaction using, for example, a dibasic acid halide and a lactam.

The dibasic acid component of this dibasic acid halide may include, for example, a linear dicarboxylic acid, such as oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, nonamethylenedicarboxylic acid or decamethylenedicarboxylic, a branched dicarboxylic acid in which a hydrogen atom in the alkylene group of a linear dicarboxylic acid is replaced by an alkyl group, cyclohexanedicarboxylic acids, aromatic dicarboxylic acids such as isophthalic acid, terephthalic acid, phthalic acid, naphthalenedicarboxylic acid, xylenedicarboxylic acid, etc.

The lactam that is reacted with the dibasic acid halide may include, for example, propiolactam, butyrolactam (2-pyrrolidone), valerolactam, ϵ -caprolactam, oenantholactam, capryllactam, pelargolactam and lauro lactam, or even lactams in a form in which the hydrogen atom of the alkylene group of these lactams is replaced by an alkyl group.

The N,N'-bisacyllactam in this invention may include, for example, N,N'-bisoxalylpyrrolidone, N,N'-bismalonylpyrrolidone, N,N'-bissuccinylpyrrolidone, N,N'-bisglutaroylpyrrolidone, N,N'-bisadipoylpyrrolidone, N,N'-bispimeloylpyrrolidone, N,N'-bissuberoylpyrrolidone, N,N'-bisazelaylpyrrolidone, N,N'-bissebacoylpyrrolidone, N,N'-decamethylenedioylpyrrolidone, N,N'-nonamethylenedioylpyrrolidone, N,N'-bisphthaloylpyrrolidone, N,N'-bisisophthaloylpyrrolidone, N,N'-

bisterephthaloylpyrrolidone, N,N'-bismethylphthaloylpyrrolidone, N,N'-bismethylisophthaloylpyrrolidone, N,N'-bismethylterephthaloylpyrrolidone, N,N'-bisisophthaloylvalerolactam, N,N'-bisterethphaloyl- ϵ -caprolactam, and N,N'-bis-2,5-dichloroterephthaloyllauro lactam. The quantity used should be selected so that the molecular weight of the polyamide obtained is 30,000 or more.

The reaction of these N,N-bisacyllactams and polyamides may be carried out at any stage of melting condition of the polyamide. For example, they may be reacted just after the polymerization of the polyamide is complete or with the melted polyamide. In addition, they may also be reacted during blow molding.

Any type of additive may be added to the modified polyamide in the method of this invention, for example, flatting agents such as titanium oxide, or stabilizers for light or heat, oxidation inhibitors, fluorescence whiteners, pigments, electric heat agents, static inhibitors, crystallization promoters, and many others.

A molecular weight of 30,000 or more for the modified polyamide in the method of this invention is necessary from the standpoint of stability of the parison. The upper limit of the molecular weight is not especially restricted, but from the standpoint of moldability, should be no more than 100,000. A suitable molecular weight range is 35,000-85,000, and 40,000-65,000 is particularly satisfactory.

The molding apparatus used for blow molding is not particularly restricted and may be a normal blow-molding apparatus. In addition, molding conditions will vary, depending

on the type of modified polyamide used, quantity of additives and the molecular weight of the modified polyamide, but should be determined to correspond to the liquid phase above the melting point of the modified polyamide, and preferably at least 10°C higher (but below the decomposition point).

Since the modified polyamide in the method of this invention has good parison stability and neither gels or becomes colored, even large blow-molded articles can be molded easily. Thus, the method of this invention is practical for a variety of actual blow-molded articles.

Application examples will be given below. In the examples, the term "parts" refers to "parts by weight," $[\eta]$ is the intrinsic viscosity measured in m-cresol at 35°C, and molecular weight was calculated on the basis of the polyamide end groups. In addition, the critical parison length is the polymer length from the extrusion opening up until the point where the extruded polymer begins to draw down. The longer this length, the better the parison stability.

Application Example 1

Production of modified polyamide in this invention

1.4 parts N,N'-bisterephthaloyl- ϵ -caprolactam were mixed with 100 parts nylon 6 chips with a terminal amino group concentration of 96.1 Eq/10⁶ g, a terminal carboxyl group concentration of 12.6 Eq/10⁶ g, a molecular weight of 1.8×10^4 , $[\eta]$ of 1.15 and a water content of 0.039 wt%. ~~Then, this was melt-extruded with an extruder~~ with a screw diameter of 30 mm and

a shaft ratio of 20 and pelletized again. The temperature of the extruder cylinder and head was 270°C.

The modified polyamide obtained had no discoloration or gelling, and had an $[\eta]$ 3.12, a terminal amino group concentration of 23.3, a terminal carboxyl group concentration of 18.2, and a molecular weight of 4.8×10^4 . The temperature dependence (Figure 1) and stress dependence (Figure 2) of the melt viscosity of this modified polyamide were measured, and the results are shown in the figures. From Figures 1-2, it is clear that the melt viscosity of the aforementioned modified polyamide in the method of this invention has a small temperature dependence, and the melt viscosity of that modified polyamide under low stress is high. It can be seen that, when this modified polyamide is used for blow molding, satisfactory blow-molded articles will be obtained.

Application Examples 2-3 and Comparative Examples 1-2

The quantities of N,N'-bisacyl- ϵ -caprolactam shown in Table I, which were produced by the method of Application Example 1, were added to polyamide, mixed and pelletized. These pellets were dried at 110°C for 16 h in a vacuum. After a water content of 0.037 wt% was obtained, the material was extruded at a rate of 2 cm/sec (2.5 g/sec) at a cylinder temperature of 250°C using a downward-blowing blow molder with a cylindrical head of 25 mm diameter. During extrusion, the parison stability was satisfactory, and absolutely no drawdown occurred.

A container (55 mm in diameter, 145 mm long cylinder, with a mouth that was 30 mm in diameter and 15 mm long) obtained in this

way was made. A cylindrical section of this container was cut out, and its hue was measured with a color meter. The results are shown in Table I. In addition, because the thickness of containers obtained in a batch with blow molding easily becomes thicker at the top and thinner at the bottom, such that there is a tendency for the thickness to become nonuniform, the thicknesses of the top and bottom sections of 10 molded articles were measured for purposes of checking uniformity. These average thickness ratios are shown in Table I as uniformity standards.

A (modified) polyamide with a molecular weight of less than 30,000 obtained using none or only a small amount of the N,N'-bisterephthaloyl- ϵ -caprolactam in the aforementioned method was used for comparison. Otherwise, pelletization and blow molding were carried out in the same way as the above, and the results of measurements done in the same way as above are shown in Table I.

Table I

Example	Quantity of N,N'-bisterephthaloyl- α -caprolactam (wt% based on polyamide)	[η]	Molecular weight of modified polyamide	Hue			Thickness ratio (top portion/bottom portion)	Critical parison length (cm)
				L	a	b		
Application Examples								
2	1.4	3.12	48×10^4	71.5	-1.4	2.1	0.998	100
3	1.0	2.51	42×10^4	72.3	-1.4	2.0	0.994	65
Comparative Examples								
1	0.5	1.88	28×10^4	70.8	-1.4	1.9	0.850	12
2	0	1.13	1.8×10^4	70.2	-1.4	2.1	Blow molding not possible	6

Application Example 4

100 parts of nylon 66 polymer with a terminal amino group concentration of $67.2 \text{ Eq}/10^6 \text{ g}$, a terminal carboxyl group concentration of $21.5 \text{ Eq}/10^6 \text{ g}$, an $[\eta]$ of 1.28 and a molecular weight of 2.3×10^4 and 1.2 parts of N,N'-bisadipoylpyrrolidone were mixed and were again melt-mixed at 280°C with an extruder.

The $[\eta]$ of the obtained polymer (modified polyamide) was 2.56, its terminal amino group concentration was $11.8 \text{ Eq}/10^6 \text{ g}$, its terminal carboxyl group concentration was $22.8 \text{ Eq}/10^6 \text{ g}$, and its molecular weight was 5.7×10^4 . This polymer was dried in a vacuum at 110°C for 16 h. After a water content of 0.052 wt% was obtained, it was blow-molded in the same way as the method of Application Example 2, and cylindrical containers were obtained. The critical parison length during blow molding was 106 cm, no coloration was seen in the container obtained, and its uniformity was satisfactory, with a thickness ratio of 0.999.

Application Examples 5-7

100 parts of polyamide of the type shown in Table II below and the N,N'-bisacyllactam shown in Table II were mixed, dried after uniformly adhering to each other, and blow-molded in the same way as the method of Application Example 2 at $250\text{--}270^\circ\text{C}$ (but only Application Example 7 had a parison extrusion rate of 10 cm/sec). The critical parison length in each case was satisfactory, 60 cm or more, no coloration was seen in the cylindrical containers obtained, and the thickness ratio was also satisfactory at 0.995-0.998.

Table II

Example	Modified polyamide				N,N'-bisacyllactam (parts)	Modified polyamide				Critical parison length (cm)
	Type of polyamide	Terminal amino group concentration (Eq/10 ⁴ g)	Terminal carboxyl group concentration (Eq/10 ⁴ g)	[η]		[η]	Molecular weight	Terminal amino group concentration (Eq/10 ⁴ g)	Terminal carboxyl group concentration (Eq/10 ⁴ g)	
Application Example 5	Nylon 6-6T copolymer (80 mol% nylon 6, 20 mol% nylon 6T)	69.8	18.8	1.33	N,N'-Bis(isophthaloyl)- ϵ -caprolactam (1.0)	2.83	4.2 x 10 ⁴	---	---	64
" 6	Nylon 12	42.9	17.6	1.58	N,N'-Bis(sebacoyl)lactam (1.0)	2.95	4.3 x 10 ⁴	18.3	28.3	64
" 7	Nylon 6	96.1	12.6	1.15	N,N'-Bis(terephthaloyl)- ϵ -caprolactam (1.5)	3.04	5.2 x 10 ⁴	17.7	20.8	67

* Molecular weight: 1.8 x 10⁴

Comparative Examples 3-4

0.75 part of vinylcyclohexenedioxide (epoxy compound) and 1.4 parts of [illegible] were added and mixed into 100 parts of nylon 6 ($[\eta] = 1.35$) chips, and these mixtures were melt-mixed during extrusion molding at 240°C.

The two types of modified polyamide obtained were dried in a vacuum at 110°C for 16 h, giving a water content of 0.042-0.046 wt%, and then blow molded according to the method of Application Example 2.

1/1, bis caprolactam
equivalent to 50.7 amine

The hue and the thickness ratio in these blow-molded items were measured, and the results are shown in Table III. In addition, the temperature dependence of the melt viscosities of the two types of modified polyamides obtained are shown in Figure 1.

Table III

Example		Quantity of epoxy compound added (parts)	[η] of modified polyamide	Hue of modified polyamide			Thickness ratio (thickness of top portion/thickness of bottom portion)
				L	a	b	
Comparative Example	3	0.75	2.32	73.0	-2.4	5.2	0.991
	4	1.40	2.52	72.8	-2.4	6.3	0.992

It can be seen from Table III that discoloration is noticeable in modified polyamide blow-molded articles when an epoxy compound is used.

Comparative Example 5

A mixture in which 2.5×10^{-4} mol phosphoric acid was added to 1 mol ϵ -caprolactam was polymerized by a conventional method. Then, the monomer was extracted with hot water and a high polymer with an [η] of 2.28 was obtained. This polymer was dried in a vacuum at 110°C for 16 h, giving a water content of 0.032 wt%, and then blow-molded according to the method of Application Example 2. There was great variation in the polymer, its melt viscosity was very high, and molding was difficult. Also, the

parison stability was poor, and, in addition, the surface of the collected molded articles was not smooth.

Comparative Example 6

A mixture in which 2.5×10^{-4} mol phosphoric acid was added to 1 mol of ϵ -caprolactam was polymerized under steam pressure, and a polymer with an $[\eta]$ of 1.38 was obtained. This polymer was heated at 180°C for 16 h in a stream of nitrogen gas, and when the polymer solidified, a polyamide with a degree of polymerization such that $[\eta]$ was 3.12 was obtained.

When this polyamide was used for blow molding, as is clear from Figure 1, the temperature dependence of the melt viscosity was high, and satisfactory molded articles were not obtained. The hue and thickness ratio of these molded articles were measured, and the results are shown in Table IV. As is clear from this table, there is noticeable coloration of the blow-molded articles, and the nonuniformity of their thickness was significant.

Table IV

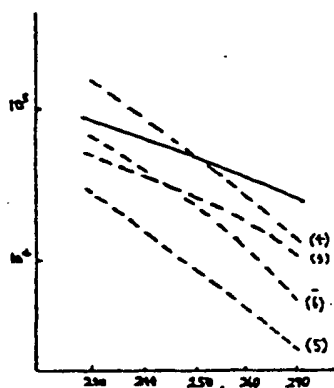
Hue			Thickness ratio (thickness of top portion/thickness of bottom portion)
L	a	b	
70.1	-2.5	6.8	0.85

4. Brief description of the figures

Figure 1 shows the temperature dependence of the melt viscosity (loading weight of 50 kg/cm² [sic]) of highly

polymerized modified polyamides obtained with the method of Application Example 2 and the highly polymerized polyamide obtained by conventional methods. Figure 2 shows the stress dependence of the melt viscosity (at a temperature of 260°C). The solid line in Figure 1 represents the modified polyamide in the method of Application Example 2, and the dotted lines represent polyamides obtained by conventional methods (comparative examples). The numerals in parentheses by the lines in Figures 1 and 2 indicate the numbers of the comparative examples.

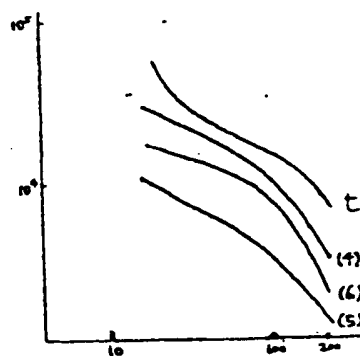
Apparent melt
viscosity (poise)



Temperature (°C)

Figure 1

Apparent melt
viscosity
(poise)



Load (kg/cm²)

Figure 2

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